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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.RESEARCHES ON THE SUBSTITUTED BENZYL COM-
POUNDS.

BY C. LORING JACKSON.

EIGHTH PAPER.

SUBSTITUTED BENZALDEHYDES.

BY J. FLEMING WHITE.

Presented April 14, 1880.

THE ortho- and parachlorbenzaldehydes are the only compounds of this class containing a single halogen atom which have been described heretofore. The former, made by Henry * from salicylaldehyde by treating it with an excess of phosphoric pentachloride and decomposing the orthochlorbenzalchloride, $C_6H_4ClCHCl_2$, formed with water in a sealed tube at 170° , was a heavy colorless oil boiling between 210° and 220° and oxidized even by the air into orthochlorbenzoic acid.

The so-called parachlorbenzaldehyde was first made by Beilstein and Kuhlberg † by boiling chlorbenzylchloride, $C_6H_4ClCH_2Cl$, with plumbic nitrate and water, according to the method of Lauth and Grimaux; ‡ also by heating chlorbenzalchloride, $C_6H_4ClCHCl_2$, with water in a sealed tube at 170° , and by treating benzaldehyde with chlorine in presence of iodine. Later, Berlin § obtained it by distilling trichlorbenzylamine, $(C_6H_4ClCH_2)_3N$, with bromine and water, and Sintenis || by the action of chlorine on chlorbenzylethylether, $C_6H_4ClCH_2OC_2H_5$. They all describe it as a heavy oil, and Berlin gives its boiling-point as 210° – 220° .

* Ber. d. ch. G., 1869, p. 135.

§ Ann. Chem. Pharm., cli. 140.

† Ann. Chem. Pharm., cxlvii. 352.

|| Ber. d. ch. G., 1871, p. 697.

‡ Ibid., cxliii. 80.

As the chlorine compounds used by Beilstein and Kuhlberg, Berlin, and Sintenis were all made by the action of chlorine on toluol in the cold, and must therefore have contained the corresponding ortho-compounds,* a revision of their work is necessary.

Parachlorbenzaldehyde, C_6H_4ClCOH , was made by boiling 10 grs. of parachlorbenzylbromide, melting-point $48\frac{1}{2}^\circ$, with 14 grs. of plumbic nitrate and 100 grs. of water for three days in a flask with a return-cooler, which was kept full of carbonic dioxide during the boiling and subsequent distillations to prevent oxidation of the aldehyde by the air. The aldehyde, separated by distillation from the plumbic bromide formed, solidified in the cooler in long white needles, which were purified by solution in acid sodic sulphite and filtering; the filtrate concentrated by evaporation deposited on cooling crystals of the double salt of the aldehyde and acid sulphite, which were washed twice with cold alcohol, dried, dissolved in a small quantity of hot water, and decomposed by distillation with solid sodic carbonate. The pure aldehyde, thus obtained, was dried over sulphuric acid in an atmosphere of carbonic dioxide and analyzed.

0.2112 gr. gave on combustion 0.4613 gr. CO_2 and 0.0680 gr. H_2O .

	Calculated for C_6H_4ClO .	Found.
Carbon	59.78	59.56
Hydrogen	3.56	3.57

Properties. Long white needles melting at $47\frac{1}{2}^\circ$, which sublime very easily; slightly soluble in water, very soluble in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. Potassic permanganate oxidizes it rapidly, air slowly, converting it into parachlorbenzoic acid.

The following substituted aldehydes were prepared from the corresponding bromides by the same method. In solubility they all resemble the parachlorbenzaldehyde.

Parabrombenzaldehyde, C_6H_4BrCOH .

0.5000 gr. of the substance gave on combustion 0.8268 gr. CO_2 and 0.1298 gr. H_2O .

	Calculated for C_6H_4BrO .	Found.
Carbon	45.40	45.10
Hydrogen	2.70	2.88

Long white needles melting at 57° . With oxidizing agents or air it forms parabrombenzoic acid.

* These Proceedings, Vol. XIV. p. 54.

Paraiodbenzaldehyde, C_6H_4ICOH .

0.7339 gr. of substance gave on combustion 0.9665 gr. CO_2 . The hydrogen was unfortunately lost.

	Calculated for C_6H_4IO .	Found.
Carbon	36.20	35.90

White needles melting at 73° . With oxidizing agents it forms paraiodbenzoic acid.

Metabrombenzaldehyde, C_6H_4BrCOH .

0.5900 gr. of substance gave on combustion 0.9800 gr. CO_2 and 0.1320 gr. H_2O .

	Calculated for C_6H_4BrO .	Found.
Carbon	45.40	45.30
Hydrogen	2.70	2.49

A colorless heavy oil, showing no signs of solidifying even in a freezing mixture of ice and salt. With oxidizing agents, or on exposure to the air, gives very easily metabrombenzoic acid.

Orthobrombenzaldehyde, C_6H_4BrCOH , was prepared from the liquid orthobrombenzylbromide, as this work was done before it had been obtained in the solid state. Instead of distilling the product of the reaction, the plumbic bromide and water were decanted while hot, leaving the aldehyde as a heavy oil, which was washed with water, purified as before described with acid sodic sulphite, dried, and analyzed.

0.5440 gr. of substance gave, on combustion, 0.8990 gr. CO_2 and 0.1476 gr. H_2O .

	Calculated for C_6H_4BrO .	Found.
Carbon	45.40	45.08
Hydrogen	2.70	3.01

A heavy colorless oil, much more rapidly oxidized by the air than any of the other substances described in this paper.

The three para-compounds yielded, when treated in alcoholic solution with sulphuretted hydrogen, the thioaldehyde, as a reddish white varnish, which it did not seem worth while to investigate.